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Coordination Chemistry of Methyl Mercury Bound in Natural Organic Matter Using Sulfur K-XANES and Mercury L_{III}-EXAFS

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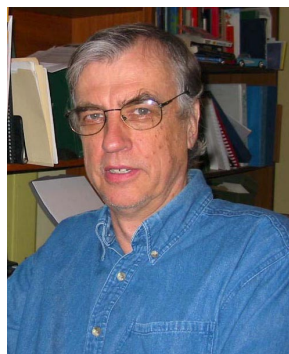
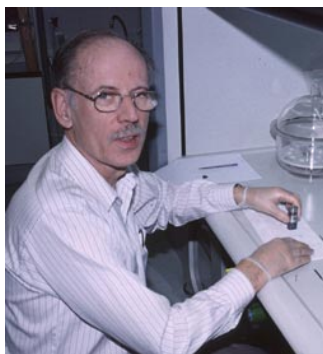
Based on results from a combination of X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy, we conclude that methyl mercury binds exclusively to high affinity reduced sulfur groups (RSH) in both stream and soil organic matter. Only when the RSH groups are saturated by methyl mercury, oxygen (or nitrogen) groups take part in the bonding. Our results suggest that approximately 25-35% of reduced sulfur in natural organic matter, as determined by XANES, is represented by RSH groups with a high affinity for methyl mercury and likely other trace metals with soft Lewis acid properties.

Combustion of fossil fuels releases mercury into the atmosphere that may be long-range transported as Hg⁰(g). After oxidation to Hg²⁺, mercury is deposited and transformed to methyl mercury (CH₃Hg) in wetlands and soils. Subsequent accumulation of the highly bioavailable methyl mercury in organisms (e.g. fish) is a severe environmental problem at northern latitudes. In order to understand mechanisms behind the formation and decomposition of methyl mercury, as well as how it is transported and made available for organisms in soils and waters, detailed information about the coordination chemistry in natural organic matter (NOM) is crucial. We combined sulfur K-edge X-ray Absorption Near Edge Spectroscopy (K-XANES) and mercury L_{III}-edge Extended X-ray Absorption Fine Structure (L_{III}-EXAFS) spectroscopy in order to determine the coordination chemistry of methyl mercury in stream and soil NOM. Sulfur XANES

was used to quantify the concentration of reduced sulfur groups (Org-S_{RED}). The same samples were added CH₃Hg to collect Hg EXAFS at varying Org-S_{RED} / CH₃Hg ratios.

Figure 1 shows the sulfur XANES spectrum for an organic soil. In the

raw data spectrum, two large peaks appear: the left one is represented by reduced sulfur and the right peak represents oxidized sulfur. Raw data were fitted by a series of Gaussian peaks, using a least-square fitting procedure. The two peaks with highest oxidation states (electronic oxidation state 5.0 and 6.0) represent sulfonates and sulfate-esters, respectively. The red peak (Org-S_{RED}) represents sulfur functionalities of importance for trace metal binding, having an average electronic oxidation state of 0.2. This peak represents the sum of functional groups such as thiol (RSH), disulfane (RSSH), sulfide (RSR) and disulfide (RSSR).



Some of the Authors of the study (clockwise from top, left): Jin Qian, P. Bloom, Wolfgang Frech, and Ulf Skjellberg.

Figure 2 shows Fourier-transformed Hg-EXAFS spectra for two NOM samples: a peat sample (FP) and dissolved organic substances gently extracted from an organic soil (PSOS). A comparison with the two peaks of the thiol resin model compound, showing a C-Hg bond (within

the methyl mercury molecule) at 1.6 Å (corresponding to a bond length of 2.03 ± 0.02 Å) and a Hg–S bond at 2.0 Å (corresponding to a bond length of 2.34 ± 0.03 Å), suggests that CH_3Hg forms one covalent bond with RSH groups in the peat and in the PSOS sample. Above a certain $\text{CH}_3\text{Hg} / \text{Org-S}_{\text{RED}}$ ratio, also oxygen (and possibly nitrogen, which cannot be separated from oxygen by EXAFS) functional groups take part in the bonding, due to a saturation of RSH groups. This is illustrated by a de-

crease of the shoulder at 2.0 Å, while the peak at 1.6 Å is broadened and slightly shifted to 1.7 Å for samples with $\text{CH}_3\text{Hg} / \text{Org-S}_{\text{RED}}$ ratios of 0.47 and 0.95. The peak at 1.7 Å represents a mixture of C–Hg and Hg–O bonds, the latter having a bond length of 2.09 ± 0.01 Å. Exact coordination numbers and bond lengths were determined by fitting of EXAFS data in k -space (not shown here).

In summary, our results show that methyl mercury binds to reduced

sulfur groups in NOM of humic streams and organic soils. A consequence of the very strong $\text{CH}_3\text{Hg-S}$ bond is that practically 100% of potentially mobile methyl mercury will be transported together with NOM in the aqueous phase and that concentrations of neutral methyl mercury forms that may pass biological membranes (e.g. CH_3HgCl , CH_3HgOH) are extremely low.

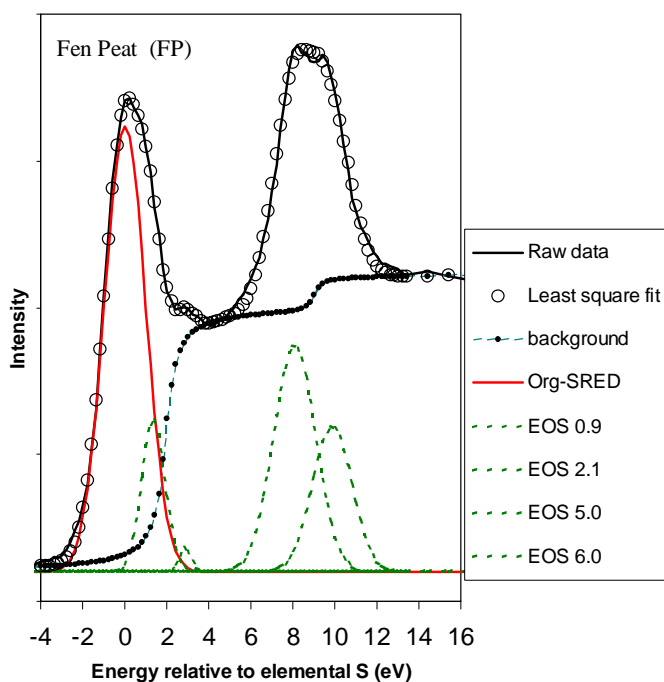


Figure 1. Sulfur K-edge XANES spectrum. The energy scale is relative to elemental sulfur (2472 eV). The raw spectrum was deconvoluted into five groups of sulfur functionalities with different electronic oxidation states (EOS).

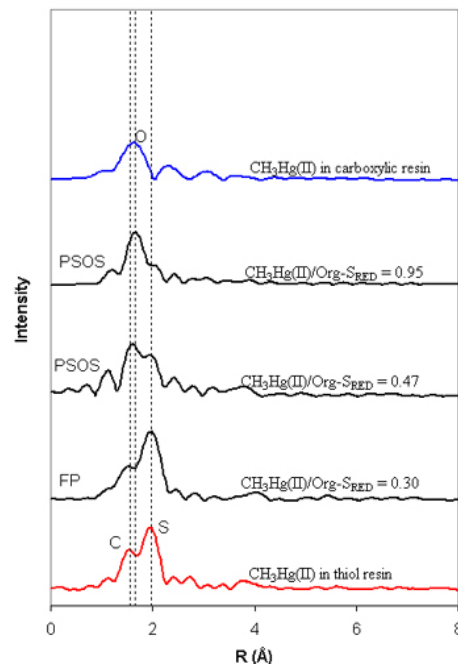


Figure 2. Fourier-transformed EXAFS spectra for two model compounds and two NOM samples. Spectra were not corrected for phase shift.